



Effects of organic silicon compounds as additives on charge–discharge cycling efficiencies of lithium in nonaqueous electrolytes for rechargeable lithium cells



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HIGHLIGHTS

- Various organic silicon compounds are prepared as electrolyte additives for lithium batteries.
- Octaphenylclosilsesquioxane exhibits highest lithium cycling efficiencies.
- Model of interface between lithium and electrolyte is proposed.

ARTICLE INFO

Article history:

Received 13 February 2014
Received in revised form
30 April 2014
Accepted 4 May 2014
Available online 14 May 2014

Keywords:

Lithium cell
Electrolyte
Organic silicon compounds
Silsesquioxane
Cycling efficiency

ABSTRACT

Influence of mixing organic silicon compounds into 1 M (M: mol L⁻¹) LiPF₆-ethylene carbonate (EC)/ethylmethyl carbonate (EMC) (mixing volume ratio = 3:7) mixed solvent electrolytes on charge–discharge cycling efficiencies of lithium metal negative electrodes is examined. As organic silicon compounds, polyether-modified siloxanes with polyethylene oxide chains, chlorotrimethylsilane, tetraethoxysilane, cis-tetra [isobutyl (dimethylsiloxy)] cyclotetrasiloxane and cage-type silsesquioxane are investigated. Charge–discharge cycling tests of lithium are galvanostatically carried out using stainless steel working electrodes. Charge–discharge cycling efficiencies of lithium tend to improve by mixing organic silicon compounds. A cage-type silsesquioxane, octaphenylclosilsesquioxane (Ph₈T₈) exhibits the highest cycling efficiency of approximately 80% with small mixing amount of 0.02 M Ph₈T₈. Mechanism of enhancement of lithium cycling efficiencies by mixing organic silicon compounds is considered to be due to the suppression of excess reduction of LiPF₆-EC/EMC by lithium and the growth of surface film on lithium.

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1. Introduction

Many of commercial lithium ion cells are composed of carbon anodes and 4V-class lithium transition metal oxide positive electrodes such as LiCoO₂ with nonaqueous electrolyte solutions. Typical example of nonaqueous electrolyte solutions is LiPF₆-EC/EMC. The improvement of energy density of lithium ion cells has been required every year. However, now the capacity of graphite negative electrodes is getting closer to the theoretical value (372 mAh g⁻¹). Then, new negative electrode materials exhibiting higher energy density than graphite have been studied. Examples

of these materials are lithium metal, various Si-based and Sn-based compounds [1]. In addition, Li/air (O₂) and Li/sulfur rechargeable cells have been studied as future generation cells [2]. At present research level, these cells generally use lithium metal anodes since original cathodes do not have lithium. However, at this stage, cycleability of lithium metal negative electrode is not sufficient for commercial use. Cycleability of lithium is mainly affected by two factors, (1) reaction between lithium and electrolyte solutions, and (2) dendrite lithium formation during electrochemical plating (charging) of lithium [3].

Reduction potentials of nonaqueous electrolyte solutions such as LiPF₆-EC/EMC are positive against lithium. Electrolyte solutions are thermodynamically reduced by lithium. Reduction products are generally solid and gas compounds. Examples of these solid compounds are lithium alkyl carbonates (RCO₂OLi, R: alkyl group),

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$(\text{CH}_2\text{OCO}_2\text{Li})_2$ and Li_2CO_3 . These solid compounds remain on lithium surface. These surface films are well known as solid electrolyte interphase (SEI) [3]. SEI is considered to be lithium ion conductor and electronic insulator. Formation of SEI makes lithium cycling efficiency less than 100% since a part of deposited lithium is consumed for SEI formation. In case of lithium metal, this SEI enhances dendrite lithium growth upon further cycling since nonuniform current distribution on lithium surface occurs. So, reaction between electrolyte solutions and lithium must be suppressed to improve cycling efficiency of lithium. When nonaqueous electrolyte solutions are used for Li/O_2 cells, Li_2CO_3 formed by degradation of electrolytes close pores of air electrodes (carbon electrodes) and makes cell performance worse [4]. The choice of electrolyte materials (solvents, solutes and additives) is one of the most important factors for charge–discharge cycling performance of lithium cells with various anodes.

Many researches on the electrolyte solutions have been carried out for improving lithium cycleability [3]. One of these researches is to modify and stabilize the chemical structure of carbonate solvents by introducing fluorine atoms. Examples of these solvents are fluoro-cyclic carbonates such as fluoro-EC, fluoro-propylene carbonate and fluoro-linear carbonates such as fluoro-methylacetate, fluoro-ethylmethyl carbonate, fluoro-diethyl carbonate, and fluoro-dimethyl carbonate [5–7]. Also, various additives for electrolyte solutions have been studied. Typical example is vinylene carbonate (VC). VC has high reduction potential and forms a good surface film on anodes such as lithium metals and carbons for the improvement of cycling efficiency [8]. Also, organosilicon compounds such as dimethylsilane [9,10] and EC with Si-contained side-chains [11] have been investigated. These organosilicon compounds exhibit similar behavior as VC does. These silanes are reactive toward lithium and produce a good surface film on lithium for enhancing stability of lithium.

In our previous works, influence of organic silicon compounds as electrolyte additives to LiPF_6 -EC/EMC on lithium cycling efficiency has been reported [12–14]. As organic silicon compounds, polyether-modified siloxanes [12] and carbonate-modified siloxanes [13,14] were examined. Chemical bonding of $\text{Si}–\text{O}$ is stronger and more stable than that of $\text{C}–\text{O}$. Lithium cycling efficiencies were improved by mixing these siloxanes. These compounds are less reactive toward lithium than LiPF_6 -EC/EMC and adsorbed on the lithium anode surface. This adsorption layer suppresses both the lithium dendrite formation and the reduction of electrolyte solutions by lithium [12]. This mechanism is similar to an addition of surfactants (surface active agents) to electrolyte solutions such as polyethyleneglycol dimethyl ethers [15]. Our previous results indicated that cycling efficiencies of lithium depended on siloxane amounts and showed maximum efficiencies around high siloxane amounts of 20–60 vol.%. Among polyether-modified siloxanes examined in previous work, diethylene glycol-(3-methyl-bis (trimethylsiloxy) silyl-2-methylpropyl) ether exhibited best lithium cycling efficiency at mixing amount of 20 vol.% [12]. Among carbonate-modified siloxanes examined in previous work, 4-(2-bis (trimethylsiloxy) methylsilyl-ethyl)-1,3-dioxolan-2-one exhibited best lithium cycling efficiency at mixing amount of 60 vol.% [13,14]. However, mixing amounts of these siloxanes are too high as additives for electrolyte solutions.

Purpose of this paper is to enhance cycling efficiency of lithium using additives for LiPF_6 -EC/EMC using organic silicon compounds as additives as small as possible. In this work, various organic silicon compounds were examined as electrolyte additives to find adequate compounds exhibiting better lithium cycling efficiency with smaller content than siloxanes previously reported.

2. Experimental

2.1. Preparation of electrolyte solutions

As base electrolyte solution, 1 M LiPF_6 -EC/EMC (3:7 in volume ratio) was used. Chemical structures of silicon compounds used here are shown in Fig. 1. As silicon compounds, polyether-modified siloxanes with polyethylene oxide chains (Fig. 1(a)–(e)), chlorotrimethylsilane (Fig. 1(f)), tetraethoxysilane (Fig. 1(g)), cis-tetra [isobutyl (dimethylsiloxy)] cyclotetrasiloxane (Fig. 1(h)) and cage-type silsesquioxanes (Ph_8T_8 , i-Bu₈T₈ and Ph_8Q_8 , Fig. 1(i)–(k)) were used. As a reference, carbonate-modified siloxane (sample B, 4-(2-bis (trimethylsiloxy) methylsilyl-ethyl)-1,3-dioxolan-2-one) was used (Fig. 1(k)). Representation of Ph_8T_8 comes from its chemical structure. Ph means R = phenyl group whose basic chemical structure is shown in Fig. 1. “T” means a unit of ternary bonding. A unit of ternary bonding is a combination of three oxygen atoms and one silicon atom. One molecule of Ph_8T_8 has 8 units of “T” and 8 phenyl functional groups. One molecule of i-Bu₈T₈ has 8 units of “T” and 8 iso-butyl functional groups. “Q” means a unit of quaternary bonding. A unit of quaternary bonding is a combination of four oxygen atoms and one silicon atom. One molecule of Ph_8Q_8 has 8 units of “Q” and 8 phenyl functional groups. These silsesquioxanes are solid at 25 °C. These cage-type organic silicon compounds are categorized as sil-sesqui-oxane (silsesquioxane) compounds. Sil, sesqui and oxane means silicon, 1.5 and oxygen, respectively. General formula of silsesquioxane compounds is $[(\text{RSiO})_{1.5}]_n$. Silsesquioxane is positioned as intermediate material or hybrid material between inorganic silicon oxide (SiO_2) and organic silicone [R_2SiO].

Polyether-modified siloxanes and carbonate-modified siloxanes were obtained from Shin-Etsu Chemicals Co. Cage-type silsesquioxanes and cis-tetra [isobutyl (dimethylsiloxy)] cyclotetrasiloxane were synthesized according to the methods reported in the previous paper [16]. Chlorotrimethylsilane, tetraethoxysilane and other organic silicon compounds were obtained from Wako Pure Chemical Co. Electrolyte solutions were prepared by mixing additives (organic silicon compounds), LiPF_6 and EC/EMC (Tomiyama Pure Chemicals Co., Lithium Battery Grade). Mixing ratio of EC/EMC was fixed as 3:7 in volume ratio. Concentration of LiPF_6 was fixed as 1 M for all ternary mixed solvent of [EC/EMC (3:7) + additive]. Hereafter, “EM” represents 1 M LiPF_6 -EC/EMC (3:7).

2.2. Charge–discharge cycling tests of lithium anodes

Charge–discharge cycling tests of lithium metal were carried out galvanostatically, using a coin cell (coin type 2032, 20 mm in diameter, 3.2 mm in thickness) with a lithium metal sheet counter electrode (0.1 mm thickness, 15 mm diameter) and a stainless steel (SUS 316) cathode case of the coin cell as the working electrode. SUS stands for steel use stainless steel. SUS 316 is relatively stable against acidic and basic compounds among various SUSs and contains 18%Cr, 12%Ni and 2.5%Mo. In charge–discharge voltage curves, charge–discharge behavior of other metals than Li is not observed. The charge–discharge cycling efficiency (coulombic efficiency, Eff) was obtained from the ratio of the stripping charge (Q_s)/plating charge (Q_p) on the stainless steel electrode. Plating Li on SUS was carried out every cycle at a charge current density of 0.5 mA cm^{−2} for 1 h. The Q_p had a constant value of 0.50 mAh cm^{−2}. Stripping of Li^+ ions (discharge) from Li deposited on SUS was carried out at a charge current density of 0.5 mA cm^{−2}. 1.5 V was used as an end point of stripping [12]. The charge–discharge current density was defined as I_{ps} . Fig. 2 shows an example of charge–discharge voltage profile of these experiments. All the electrochemical measurements were carried out at 25 °C.

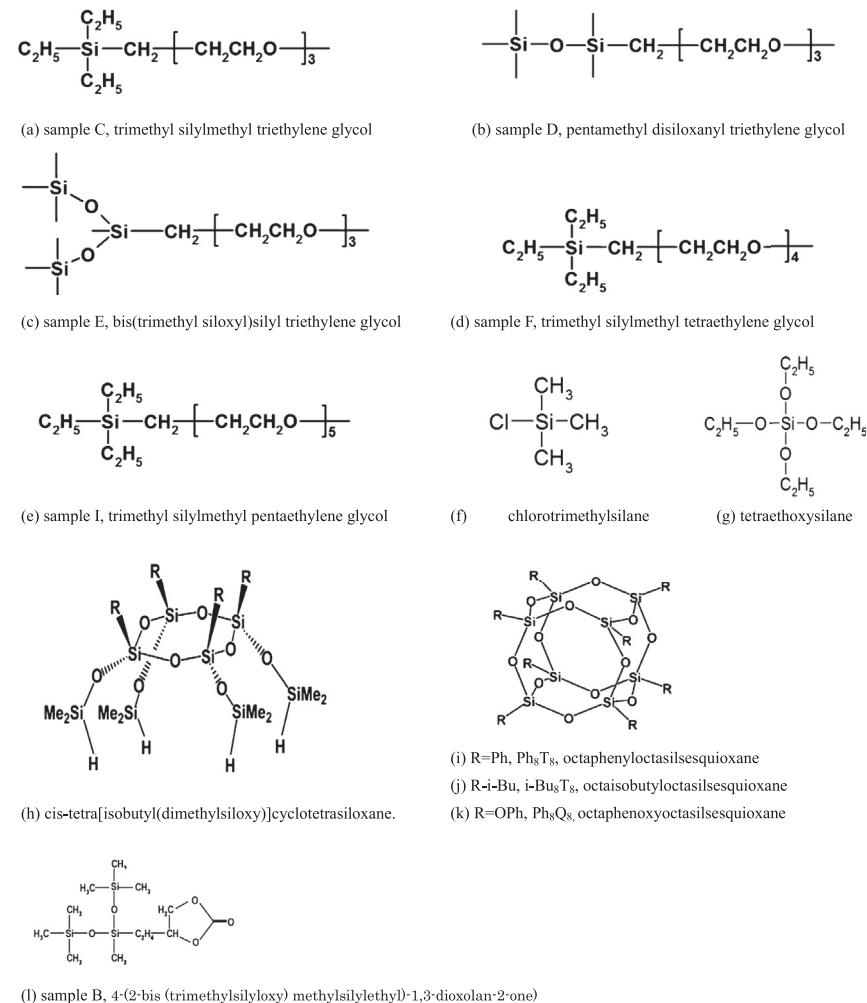


Fig. 1. Chemical structure of organic silicon compounds.

3. Results and discussion

3.1. Preliminary tests of organic silicon compounds as electrolyte additives

Purpose of this work is to find organic silicon compounds providing high lithium cycling efficiency by small amounts of addition to base electrolyte solutions. First, preliminary tests were carried out to search for suitable basic molecular structure of organic silicon compounds exhibiting lithium cycling efficiency as high as possible with small amounts. Charge–discharge cycling

efficiencies of lithium were measured as preliminary screening tests to investigate ability of various organic silicon compounds with different molecular structure. As electrolyte solutions, 1 M LiPF₆–EC/EMC (3:7) + various organic silicon compounds (additives) were used. Coin cells consisted of lithium (Li) anodes and SUS cathodes were utilized for cycling tests of lithium. As silicon compounds, polyether-modified siloxanes with polyethylene oxide chains (Fig. 1(a)–(e)), chlorotrimethylsilane (Fig. 1(f)), tetraethoxysilane (Fig. 1(g)), cis-tetra[isobutyl(dimethylsiloxy)]cyclotetrasiloxane (Fig. 1(h)) and cage-type silsesquioxane (Ph₈T₈) (Fig. 1(i)) were used. As a reference, carbonate-modified siloxane (sample B, 4-(2-bis(trimethylsiloxy)methylsilylethyl)-1,3-dioxolan-2-one) was used (Fig. 1(k)).

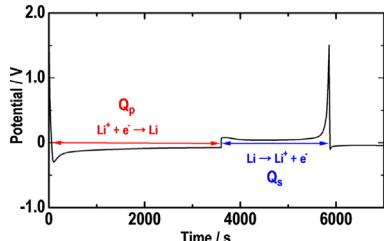


Fig. 2. Charge–discharge voltage profile of lithium, 1 M LiPF₆–EC/EMC (30:70 vol.%), SUS working electrode; I_{ps}: 0.5 mA cm⁻², Q_p: 0.5 mAh cm⁻², discharge cut-off voltage: 1.5 V.

3.1.1. Polyether-modified siloxanes

Five polyether-modified siloxanes (samples C, D, E, F and I shown in Fig. 1) were tested. Chemical structures of these compounds are shown in Fig. 1(a)–(e). Fig. 3 shows relation between average lithium cycling efficiencies from first to 30th cycle (coulombic efficiency_{Ave.30}) and addition amounts (siloxane content) of polyether-modified siloxanes (samples C, D, E, F and I). Lithium cycling efficiencies in EM + siloxanes were higher than that in EM alone. When relatively small amounts of siloxanes (10 and 20 vol.%) are mixed, lithium cycling efficiency tends to increase with an increase in an ether chain number. When relatively high

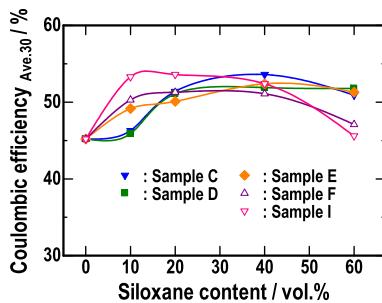


Fig. 3. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without samples C, D, E, F and I.

amounts of siloxanes (40 and 60 vol.%) are mixed, lithium cycling efficiency tends to decrease with an increase in an ether chain number. These results suggest that ether chain number directly affects adsorption state of siloxanes on the interface between anode and electrolyte. This discussion is guess from results about adsorption state of surfactants of polyethyleneglycol dimethyl ethers [15].

Fig. 4 shows relation between coulombic efficiency_{Ave.30}, number of polyethylene oxide chains (ether chain number) and addition amounts of polyether-modified siloxanes with the same functional groups of (C₂H₅)₂SiCH₂ (samples C, F and I). Average efficiencies in EM + siloxanes were higher than that in EM alone. EM + sample I (10 vol.%) shows 8% higher efficiency than that of EM alone.

However, relatively high amounts of siloxanes (10–60 vol.%) are needed for improvement of lithium cycling efficiency in case of these polyether-modified siloxanes examined here. In addition, highest values of cycling efficiencies (53%) are lower than those of carbonate-modified siloxanes (67%) (sample B, Fig. 5) previously reported [14]. Unfortunately these polyether-modified siloxanes do not meet purpose of this work.

3.1.2. Various organic silicon compounds

Fig. 6 shows results of lithium charge–discharge cycling tests in EM with and without various organic silicon compounds. EM + these silicon compounds exhibited similar or higher cycling efficiencies by very small addition amounts of 0.05–0.20 mol L⁻¹ (0.04–0.16 vol.%) compared with that in EM alone. Specific densities of these silicon compounds are in the range between 1.00 and 1.28. Chlorotrimethylsilane is reported to be effective for improvement of lithium cycling efficiency as surface modification agent on lithium [10]. However, lithium cycling efficiency in EM + chlorotrimethylsilane was a little bit lower than that in EM alone. Simple mixing of chlorotrimethylsilane into EM

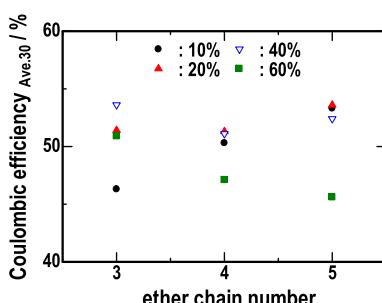


Fig. 4. Relation between average coulombic efficiency, ether chain number, and amounts of additives, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without samples C, F and I.

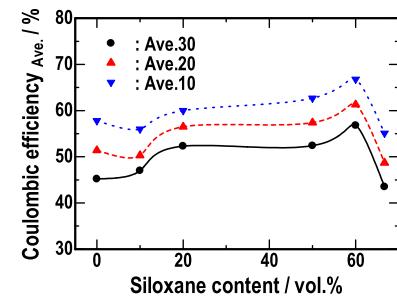


Fig. 5. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without sample B.

does not enhance lithium cycling efficiency. cis-tetra [isobutyl(dimethylsiloxy)] cyclotetrasiloxane exhibited similar cycling efficiency to that in EM alone. Tetraethoxysilane showed a little bit higher cycling efficiency.

The most important result obtained in Fig. 6 is that Ph₈T₈ showed drastic enhancement of lithium cycling efficiency with extremely small mixing amount (0.20 mol L⁻¹, 0.16 vol.%). This efficiency (approximately 80%) is obviously higher than that (approximately 67%) of EM + modified carbonate siloxane (mixing amounts of 60 vol.%) previously reported [14]. This performance of Ph₈T₈ meets the purpose of this work. This effect of Ph₈T₈ may be closely related to large number of Si–O bonding per one Ph₈T₈ molecule and its adsorption state on anode/electrolyte interface based on cage-type structure. So, more detailed investigation of cage-type organic silicon compounds was carried out.

3.2. Charge–discharge cycling properties of lithium in electrolyte solutions with cage-type organic silicon compounds

Three cage-type organic silicon compounds were examined. These are Ph₈T₈, i-Bu₈T₈ and Ph₈Q₈. Ph or i-Bu means R = phenyl or R = *i*-butyl whose basic chemical structure is shown in Fig. 1(i) or (k). “T” means a unit of ternary bonding and “Q” means a unit of quaternary bonding as already explained in Section 2. These cage-type organic silicon compounds are categorized as silsesquioxane compounds.

3.2.1. Ph₈T₈

3.2.1.1. Charge–discharge cycling properties of lithium in electrolyte solutions with Ph₈T₈. Fig. 7 shows relation between coulombic efficiencies (charge–discharge cycling efficiencies of lithium), charge–discharge cycle number and mixing amounts of Ph₈T₈ in EM + Ph₈T₈. Efficiencies in EM + Ph₈T₈ tend to be higher than that in EM alone. Fig. 8 shows relation between mixing amounts of

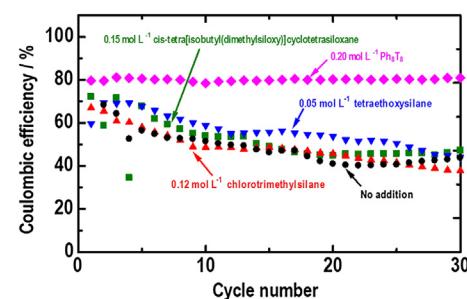


Fig. 6. Charge–discharge cycle behavior of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without chlorotrimethylsilane, chlorotrimethylsilane, tetraethoxysilane, cis-tetra[isobutyl(dimethylsiloxy)] cyclotetrasiloxane and Ph₈T₈.

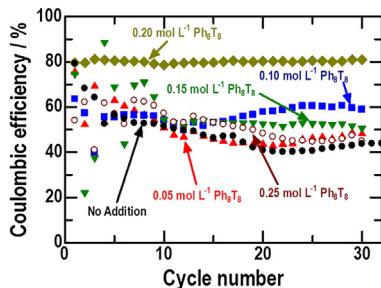


Fig. 7. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without Ph₈T₈.

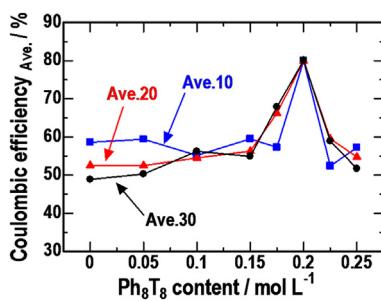


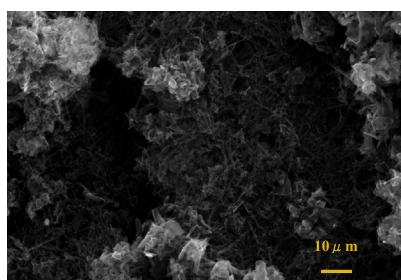
Fig. 8. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without Ph₈T₈.

Ph₈T₈ in EM + Ph₈T₈ and average coulombic efficiencies from first to 10th cycle (Ave.10), to 20th cycle (Ave.20) and to 30th cycle (Ave.30). Efficiencies depend on amounts of Ph₈T₈. Average efficiencies of Ave.10, Ave.20 and Ave.30 exhibited the maximum efficiencies of approximately 80% at 0.20 M Ph₈T₈. These average efficiencies (approximately 80%) are obviously higher than those in EM alone (50–60%). From these results, it is found that there is adequate amount of Ph₈T₈ to obtain the maximum efficiency. This tendency is similar to those obtained in case of polyether-modified siloxanes [12] and carbonate-modified siloxanes examined in previous works [14]. A distinct difference between Ph₈T₈ and siloxanes previously examined is mixing amount of organic silicon compounds exhibiting the maximum efficiency. Adequate amount of 0.20 M (0.16 vol.%) in case of Ph₈T₈ is drastically lower than those of polyether-modified siloxanes (10–20 vol.%) and carbonate-modified siloxanes (40–60 vol.%). This difference may be caused from the fact that one molecule of Ph₈T₈ has larger number of Si–O–Si units and covers wider surface area of anode than other siloxanes do. The fundamental mechanism for enhancement of lithium cycling efficiency should be the same as those of polyether-modified siloxanes and carbonate-modified siloxanes.

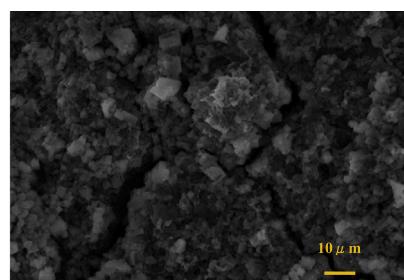
3.2.1.2. Morphology of electrochemically deposited lithium. Morphology of deposited lithium was observed by following process. Li/SUS coin cells with and without Ph₈T₈ were disassembled in argon gas filled dry box after 30th charging. The SUS electrodes were washed with EC/EMC (3:7 in volume ratio) solvents and dried in vacuum for 10 min at 25 °C. Then, SEM (scanning electron microscope) observation was carried out for these lithium-deposited SUS electrodes to investigate morphology of electrochemically deposited lithium (Fig. 9). In EM alone, deposition of lithium is not uniform over working electrode surface. When 0.02 M Ph₈T₈ + EM was used, lithium deposition is more uniform and smoother than that in EM alone. In addition, solid compound is observed between deposited lithium particles covered with SEI when 0.02 M Ph₈T₈ + EM was used. This compound is not observed in case of EM alone. This solid compound is considered to be Ph₈T₈ itself. Ph₈T₈ may exist as a part of SEI composition. Main chemical components of SEI are reduction products of EM by lithium. This prediction will be discussed in more detail in the next sections of XRD and FT-IR measurements. Mixing Ph₈T₈ is effective on smooth lithium deposition and suppresses nonuniform current distribution on electrode surface. A decrease in degree of roughness of lithium deposition morphology (a decrease in reaction surface area) is effective for a decrease in reaction amount of electrolyte solution with lithium (suppression of growth of SEI and of consumption of lithium).

3.2.1.3. XRD measurements of electrochemically deposited lithium. Li/SUS coin cells with and without Ph₈T₈ were disassembled in argon gas filled dry box after 30th charging. Lithium-deposited SUS electrodes were washed with EC/EMC (3:7 in volume ratio) solvents and dried in vacuum for 10 min at 25 °C. Then, XRD (X-ray diffraction) was carried out for lithium-deposited SUS electrodes to get information about SEI (Fig. 10). Also XRD pattern of Ph₈T₈ itself is shown in Fig. 10 as reference sample. XRD results indicate that all samples except for Ph₈T₈ itself show almost the same peaks related to Li. XRD results also indicate that all samples with 0.05–0.25 M Ph₈T₈ and Ph₈T₈ itself except for EM alone show peaks of SiO₂ in the same positions originated from inorganic framework of SiO₂ in Ph₈T₈. These results suggest that Ph₈T₈ exists without reacting (as same state of starting material) in SEI of deposited lithium. This discussion agrees to that of SEM results for deposited lithium.

3.2.1.4. Chemical composition of SEI on lithium. SEI is formed by reduction of electrolyte solutions by lithium [17]. SEI is composed of many organic and inorganic compounds [17–19]. Typical compounds are lithium alkyl carbonates (RCO₂Li), (CH₂OCO₂Li)₂ and Li₂CO₃ for cyclic carbonates such as EC. SEI in linear cycling carbonates such as EMC contains similar compounds of lithium alkoxide (ROLi), RCO₂OLi, (CH₂OCO₂Li)₂ and Li₂CO₃. Typical reactions between Li and electrolyte solutions are shown in equations



(a) EM alone (x 1000)



(b) EM + 0.20 M Ph₈T₈ (x 1000)

Fig. 9. SEM images of deposited lithium after 30th charge, 1 M LiPF₆-EC/EMC (30:70 vol.%), with and without Ph₈T₈.

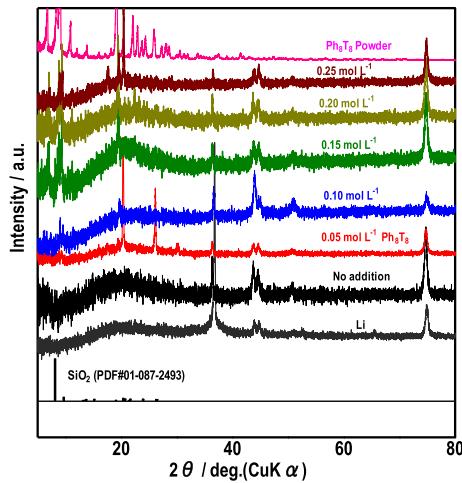


Fig. 10. X-ray diffractogram of the lithium after 30th charge, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without Ph₈T₈.

(1)–(5). There are several ways of production process of Li₂CO₃ [17,19]. For instance, Li₂CO₃ is produced from decomposition of (CH₂OCO₂Li)₂ (equation (2)) [19]. According to equations (1) and (3), organic components (CH₂OCO₂Li)₂ form first on surface of electrodes and gradually changes to inorganic components (Li₂CO₃) with an increase in standing or charging time. As a result, organic components exist on surface of SEI and inorganic components exist inside SEI (near electrodes) as reported by study on chemical analysis in depth direction of SEI [19]. When reduction of electrolyte solutions by lithium is large, large amounts of organic components may be detected in SEI.

FT-IR spectroscopy was carried out to investigate chemical composition of SEI on lithium anode surface in EM + Ph₈T₈ (0.05–0.25 M). IR samples were prepared as follows. Li/SUS coin cells were fabricated with EM + Ph₈T₈. Also Li/SUS coin cell was fabricated with EM alone as reference. These cells were cycled 30 times. Cells were disassembled in argon gas filled dry-box after plating lithium on SUS. These working electrodes (SUS with plated lithium) were washed with EC/EMC (3:7 in volume ratio) solvents and dried in vacuum for 10 min at 25 °C. IR analyzed SEI films of these working electrodes.

Fig. 11 shows IR spectroscopy results. SEI films prepared with (0.05–0.25 M) and without Ph₈T₈ show IR peaks exhibiting

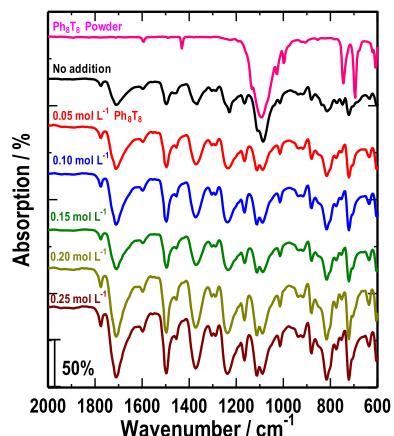


Fig. 11. Infrared absorption spectra of SEI of lithium surface after 30th charge, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without Ph₈T₈.

ROCO₂Li or (ROCO₂Li)₂ and Li₂CO₃. ROCO₂Li or (ROCO₂Li)₂ shows IR peaks around 800–850 cm⁻¹, 1630–1690 cm⁻¹ and 1300–1350 cm⁻¹ [19]. Separation of these peaks for two compounds is almost impossible. Li₂CO₃ shows IR peaks around 1504 cm⁻¹, 1430 cm⁻¹ and 870 cm⁻¹ [19]. 1750–1800 cm⁻¹ corresponds to C=O vibration. It may correspond to ROCO₂Li or (ROCO₂Li)₂. However, it is hard to identify this peak. IR spectra of SEI with Ph₈T₈ show peaks corresponding SiOSi (1000–1130 cm⁻¹) and peaks corresponding SiPh (690–700 cm⁻¹, 710–760 cm⁻¹, 1430 cm⁻¹ and 1590–1600 cm⁻¹). As XRD and SEM results show, Ph₈T₈ exists in SEI without reaction after cycles. There is a difference in shapes of peaks around 1100 cm⁻¹ between with and without silicon compounds after cycles though position of these two peaks are similar. Difference of these peaks between with and without silicon compounds after cycles may result from complex formation between silicon compound and SEI. From IR spectroscopy, following results are obtained. First, main chemical components of SEI are produced from reduction of EC/EMC by lithium both for with and without Ph₈T₈. Second, ratio of amounts of inorganic compounds (Li₂CO₃) to those of organic compounds of ROCO₂Li or (ROCO₂Li)₂ in SEI with Ph₈T₈ is larger than that of electrolyte solution without Ph₈T₈. When ratio of peak area of [inorganic compounds/organic compounds] is calculated from IR results, the ratio is 0.445 in EM alone and 0.646 in EM + 0.02 M Ph₈T₈, respectively. Third, SEI with Ph₈T₈ shows peaks of Ph₈T₈ itself even after washing with EC/EMC. Ph₈T₈ still remains in SEI without reduction or oxidation even after cycles. These results suggest that Ph₈T₈ is captured in solid SEI and this special SEI structure may suppress excess reaction of electrolyte solutions by lithium. These results agree to the interfacial model proposed in previous works on modified polyether-modified siloxanes and carbonate-modified siloxanes [12,14].

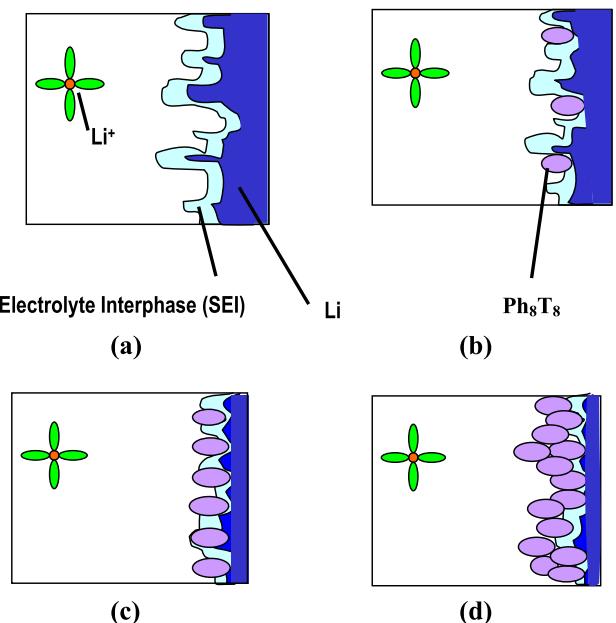
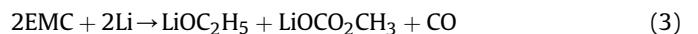
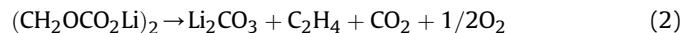
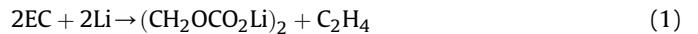


Fig. 12. Schematic model of SEI with and without Ph₈T₈.

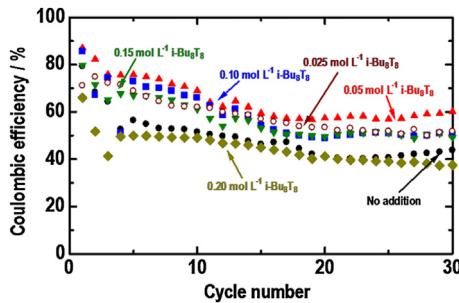


Fig. 13. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without i-Bu₈T₈.

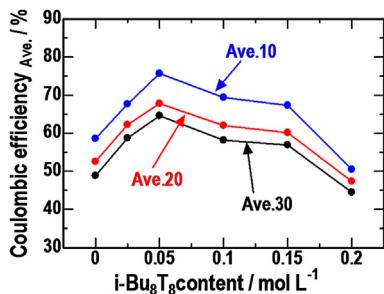
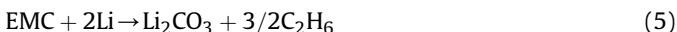


Fig. 14. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without i-Bu₈T₈.



3.2.1.5. Model for interface between lithium electrode and electrolyte solutions. Summarizing the results of lithium cycling efficiency measurements, morphology of lithium deposition, XRD and FT-IR results for SEI of lithium, the following mechanism may be proposed for the improvement of lithium cycling efficiency by addition of Ph₈T₈. This mechanism is the same as that reported in the previous works [9,10]. **Fig. 12** shows the proposed models for cycling

efficiency enhancement by adding Ph₈T₈ (please see **Fig. 8** as well). Just after charging (lithium deposition), freshly deposited lithium is chemically active. On the lithium surface, EM is chemically reduced by lithium and produces the surface film. Reduction products were reported to be solid compounds and gas compounds [18,19]. Solid compounds remained on the lithium produce SEI. **Fig. 12(a)**: By no addition of Ph₈T₈, surface film is composed of reduction products of EM. **Fig. 12(b)**: By small addition of Ph₈T₈, surface film is mainly composed of reduction products of EM. Small amounts of Ph₈T₈ is involved in SEI or it adsorbs on SEI surface. Ph₈T₈ is less reactive than EM. **Fig. 12(c)**: By medium amounts of Ph₈T₈ (0.20 M), the surface film is thin and is composed of both the reduction product of EM and Ph₈T₈. **Fig. 12(d)**: By adding larger amounts of Ph₈T₈, excess and thick Ph₈T₈ layer exists around lithium electrode. This excess Ph₈T₈, electronic insulator may be resistive for smooth charge–discharge of lithium and lithium ion diffusion. Then, lithium cycling efficiency improves by adding Ph₈T₈ and shows the maximum value against addition amounts of Ph₈T₈.

3.2.2. i-Bu₈T₈

3.2.2.1. Charge–discharge cycling properties of lithium in electrolyte solutions with i-Bu₈T₈. Influence of another cage-type organic silicon compound, i-Bu₈T₈ on charge–discharge efficiencies (coulombic efficiencies) of lithium was examined. **Fig. 13** shows relation between coulombic efficiencies, charge–discharge cycle number and mixing amounts of i-Bu₈T₈ in EM + i-Bu₈T₈. **Fig. 14** shows relation between mixing amounts of i-Bu₈T₈ in EM + i-Bu₈T₈ and average coulombic efficiencies from first to 10th cycle (Ave.10), to 20th cycle (Ave.20) and to 30th cycle (Ave.30). Efficiencies depend on amounts of i-Bu₈T₈. Average efficiencies tend to be higher than that of EM alone in the range of 0.05 and 0.15 M i-Bu₈T₈ addition. At 0.20 M i-Bu₈T₈ addition, efficiencies were a little lower than those of EM alone. Average efficiencies exhibited the maximum value at 0.05 M i-Bu₈T₈. These average efficiencies (65–75%) are higher than those in EM alone (50–60%). Adequate amount of 0.05 M (0.04 vol.%) i-Bu₈T₈ is considerably lower than those of modified polyether-modified siloxanes (10–20 vol.%) and carbonate-modified siloxanes (40–60 vol.%). This tendency is similar to that obtained in case of Ph₈T₈.

3.2.2.2. Morphology of electrochemically deposited lithium. Morphology of electrochemically deposited lithium in EM with and without i-Bu₈T₈ was investigated (**Fig. 15**). When 0.05 M i-

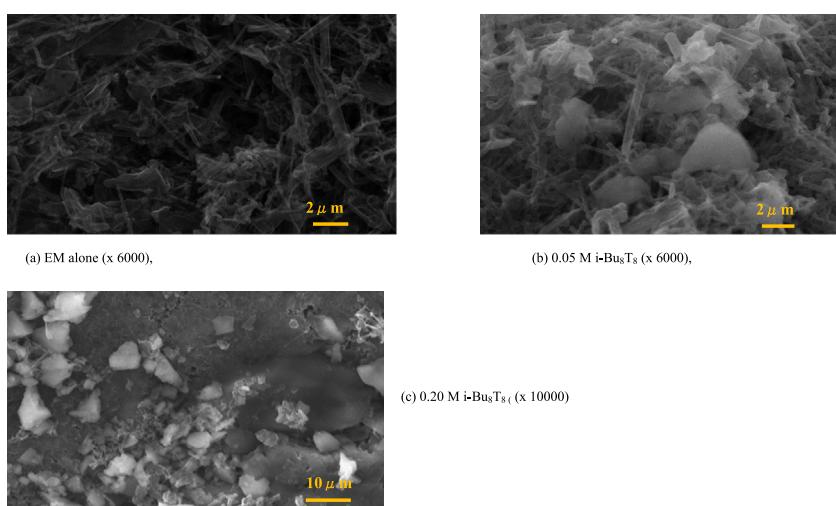


Fig. 15. SEM images of deposited lithium after 30th charge, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without i-Bu₈T₈.

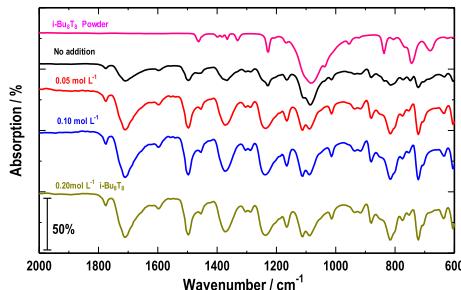


Fig. 16. Infrared absorption spectra of SEI of lithium surface after 30th charge, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without i-Bu₈T₈.

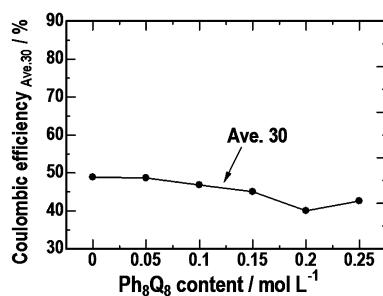


Fig. 17. Average coulombic efficiency of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without Ph₈Q₈.

Bu₈T₈ + EM was used, lithium deposition is more uniform and smoother than EM alone. 0.05 M i-Bu₈T₈ solution exhibited higher efficiency than that of EM alone. When 0.20 M i-Bu₈T₈ + EM was used, lithium deposition is not smooth. Efficiency did not improve in 0.20 M i-Bu₈T₈ solution. In both 0.05 M and 0.20 M solutions, solid compound is observed between deposited lithium particles with SEI. This solid compound is considered to be i-Bu₈T₈ itself as in case of Ph₈T₈. In cases of 0.20 M, excess i-Bu₈T₈, electronic insulator exists. This phenomenon makes nonuniform current distribution and lithium deposition worse. This result may be closely related to poor lithium cycling efficiency in excess addition of i-Bu₈T₈.

3.2.2.3. Chemical composition of SEI on lithium. Fig. 16 shows IR spectroscopy results for SEI films on lithium prepared with and without i-Bu₈T₈. As in case of IR results for Ph₈T₈, i-Bu₈T₈ exists in SEI without reaction. These results suggest that i-Bu₈T₈ is captured in solid SEI and this special SEI structure may suppress excess reaction of electrolyte solutions by lithium.

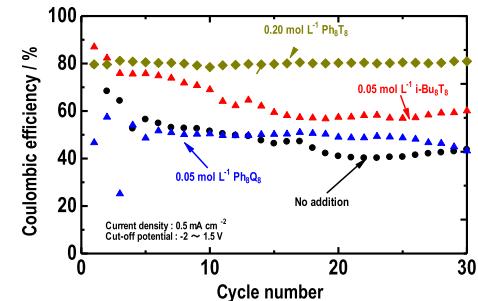


Fig. 19. Coulombic efficiencies of lithium, 1 M LiPF₆-EC/EMC (30:70 vol.%) + cage-type compounds.

3.2.3. Ph₈Q₈

3.2.3.1. Charge-discharge cycling properties of lithium in the electrolyte solutions with Ph₈Q₈. Influence of another cage-type organic silicon compound, Ph₈Q₈ on charge-discharge efficiencies (coulombic efficiencies) of lithium was examined. Fig. 17 shows relation between average coulombic efficiencies (Ave.30) and mixing amounts of Ph₈Q₈ in EM + Ph₈Q₈. With an increase in Ph₈Q₈ amount, efficiency tends to decrease. Average efficiencies in EM + Ph₈Q₈ are lower than that of EM alone. Fig. 18 shows morphology of deposited lithium after 30th charge. Obviously larger particles exist on anode surface than those in EM + Ph₈T₈ or i-Bu₈T₈. Large particles are Ph₈Q₈ itself because Ph₈Q₈ exists in SEI without oxidation or reduction like in cases of EM + Ph₈T₈ and i-Bu₈T₈. More nonuniform current distribution is made on electrode surface by mixing Ph₈Q₈ to EM than EM alone since Ph₈Q₈ is electronic insulator. Then, decrease in lithium cycling efficiency by mixing Ph₈Q₈ may be caused by worse lithium deposition morphology resulted from more nonuniform current distribution.

4. Conclusion

Fig. 19 shows best lithium cycling efficiencies of 1 M LiPF₆-EC/EMC (30:70 vol.%) + three cage-type organic compounds examined in this work. The highest improvement of lithium charge-discharge cycling efficiencies was obtained by very small mixing of Ph₈T₈ (0.20 M) in LiPF₆-EC/EMC. Efficiencies are high in the order of Ph₈T₈ > i-Bu₈T₈ > no addition > Ph₈Q₈. Ph₈T₈ covers more uniformly than i-Bu₈T₈. A decrease in lithium cycling efficiency by mixing Ph₈Q₈ may be caused by worse lithium deposition morphology resulted from existence of large Ph₈Q₈ and more nonuniform current distribution. Mechanism of enhancement of lithium cycling efficiencies by mixing Ph₈T₈ is considered to be due to the suppression of excess reduction of LiPF₆-EC/EMC by lithium (growth of surface film (SEI) on lithium) and relatively smoother lithium deposition morphology. XRD and IR studies indicate that

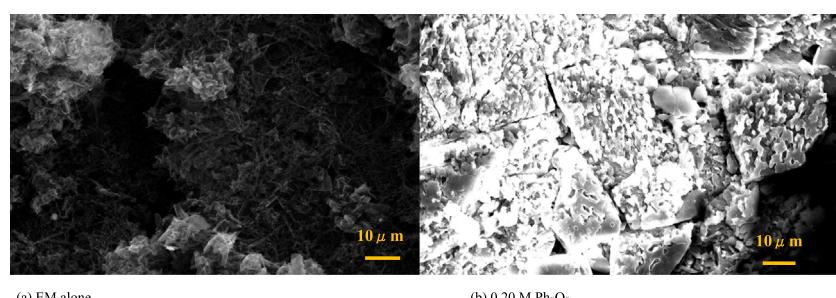


Fig. 18. SEM images of deposited lithium after 30th charge, 1 M LiPF₆-EC/EMC (30:70 vol.%) with and without Ph₈Q₈.

SEI formed in electrolyte solutions mixed with organic silicon compounds contains organic silicon compounds without reacting and more inorganic compounds than those by LiPF₆-EC/EMC alone. By modifying chemical structure of organic silicon compounds, we expect to obtain the more improvement of charge–discharge cycling performance for various lithium-based negative electrode materials.

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